Full length article

Enhancing performance and surface antifouling properties of polysulfone ultrafiltration membranes with salicylate-alumoxane nanoparticles

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ABSTRACT

To improve the hydrophilicity and antifouling properties of polysulfone (PS) ultrafiltration membranes, we studied the use of salicylate-alumoxane (SA) nanoparticles as a novel hydrophilic additive. The effects of SA nanoparticles on the membrane characteristics and performance were investigated in terms of membrane structure, permeation flux, solute rejection, hydrophilicity, and antifouling ability. The new mixed-matrix membranes (MMMs) possess asymmetric structures. They have smaller finger-like pores and smoother surfaces than the neat PS membranes. The embedment of SA nanoparticles in the polymer matrix and the improvement of surface hydrophilicity were investigated. Ultrafiltration experiments indicated that the pure-water flux of the new MMMs initially increases with SA nanoparticles loading followed by a decrease at high loadings. Higher BSA solution flux was achieved for the MMMs compared to the neat PS membranes. Membranes with 1 wt.% SA nanoparticles exhibit the highest flux recovery ratio of 87% and the lowest irreversible fouling of 13%.

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1. Introduction

Ultrafiltration (UF) is a membrane separation process driven by pressure difference [1,2]. It has been employed for the removal of various components such as macromolecules, proteins, and viruses from different solutions [3,4], in food processing, water and wastewater treatment and seawater desalination [5,6]. Low operating costs, high flux, satisfactory permeate quality, and simplicity are some advantages of UF over other membrane technologies [7,8].

The physical and chemical properties of polymers used in manufacturing UF membranes have strong effects on the structure and performance of the membranes [9,10]. Examples of such polymers are polysulfone (PS) [11], polyethersulfone (PES) [12], cellulose acetate (CA) [13], polyvinylidene fluoride (PVDF) [14], polyacrylonitrile (PAN) [15], polyethylene (PE), polypropylene (PP), and polyamide and polyimide [16]. Among these, PS is widely used due to its appealing physicochemical characteristics such as high

thermal stability, adequate mechanical strength, high chemical resistance over a wide range of pH, and excellent film forming ability for UF applications [17,18]. However, a major disadvantage of PS is its hydrophobic nature, which causes membrane fouling [19,20]. Membrane fouling can be influenced by membrane characteristics, feed solution properties and operation conditions [21]. Typically, smooth and highly hydrophilic surfaces resist fouling [22]. Therefore, to improve membrane resistance against fouling, the surface hydrophilicity of the membrane should be improved [23]. Various methods have been applied to improve the surface hydrophilicity of UF membranes. Among them, incorporation of hydrophilic nanoparticles into polymer matrix is an effective way of providing membranes with adequate fouling resistance [24,25].

To prepare nanocomposite membranes, various nanoparticles such as titania (TiO_2) [26], mesoporous silica (SiO_2) [27], SiO_2–GO [28], alumina (Al_2O_3) [4], zirconia (ZrO_2) [29], zinc oxide (ZnO) [20], silver (Ag) [30], zeolite [31], and multi-walled carbon nanotubes [7,32] have been used. Arsuaga et al. [33] investigated the effect of metal oxide nanoparticles on the morphology and performance of nanocomposite membranes. They found that the presence of nanoparticles in the casting solution decreases contact angle, increases water flux, and improves fouling resistance. Vatanpour

et al. [34] studied the antifouling properties of MMMs incorporated with boehmite nanoparticles. The addition of boehmite nanoparticles to the membranes changed the structure and morphology of the resulting membranes and created more hydrophilic and smoother surfaces, leading to a substantial increase in the solution flux and flux recovery ratio. While there have been many studies on modifying PSUF membranes using various hydrophilic nanoparticles, to best of our knowledge, there has been no reported study of using SA nanoparticles in the PS casting solution. SA nanoparticles form a stable inorganic material that is inexpensive, non-toxic, and resistant to chemical cleaning agents. Our expectation was that the addition of SA nanoparticles improves the hydrophilicity and surface properties, and decreases fouling of the MMMs due to the extra OH groups on their surfaces.

In this work, we aimed to fabricate novel PS/SA- UF membranes with satisfactory antifouling properties. To achieve this, we synthesized SA nanoparticles and loaded them into PS to fabricate high performance MMMs via the phase inversion method. Finally, the characteristics, structure, and morphology of the fabricated membranes were studied.

2. Materials and methods

2.1. Materials

Aluminum nitrate 9-hydrate [Al $(NO_3)_3 \cdot 9H_2O$] and sodium hydroxide (NaOH) supplied by Merck (Germany) and salicylic acid obtained from Scharlau (Germany) were used for the synthesis of boehmite and SA nanoparticles. Polysulfone (PS, Mw 35000 g/mol) provided by Solvay was used as the base polymer for the preparation of the mixed membranes. *N,N*-dimethylacetamide (DMAc, 99.8%) as the polymer solvent, Triton ×100 and sodium dodecyl sulfate (SDS) as surfactants, polyethyleneglycol (PEG) with a molecular weight of 400 Da as the pore former, and bovine serum albumin (BSA, MW ∼66 kDa) as a model protein for fouling tests were purchased from Merck (Germany).

2.2. Preparation of boehmite nanoparticles

Boehmite nanoparticles were synthesized according to the procedure described in Ref. [35]. A brief summary of the procedure we used is as follows. First two solutions were made: a NaOH solution by dissolving 6.490 g of NaOH in 50 ml of distilled water, and an Al(NO$_3$)$_3 \cdot$9H$_2$O solution by dissolving 20 g of Al(NO$_3$)$_3 \cdot$9H$_2$O in 30 ml of distilled water. The sodium hydroxide solution was then gradually added to the Al (NO$_3$)$_3 \cdot$9H$_2$O solution at a rate of 2.94 ml/min, while the aluminum nitrate solution was stirred. The resulting milky solution was mixed and sonicated in an ultrasonic bath at 25 °C for 3 h. The mixture precipitate was then filtered out using a filter paper, washed with distilled water, and finally dried in an oven at 220 °C for 4 h.

2.3. Synthesis of salicylate alumoxane nanoparticles

Salicylate alumoxane (SA) nanoparticles were synthesized from the reaction between boehmite nanoparticles and salicylic acid using the procedure described next [36]. First, 6 g of boehmite nanoparticles and 12 g of salicylic acid were dissolved in 200 ml of distilled water. The resulting suspension was sonicated in the ultrasonic bath at 25 °C for 10 min and then refluxed at its boiling point. Next, the mixture was cooled to the room temperature, and filtered. To remove the unreacted salicylic acid, the precipitate was mixed with 200 ml of ethanol. The resulting mixture was filtered and kept in an oven at 60 °C. Fig. 1 shows the reactions involved in
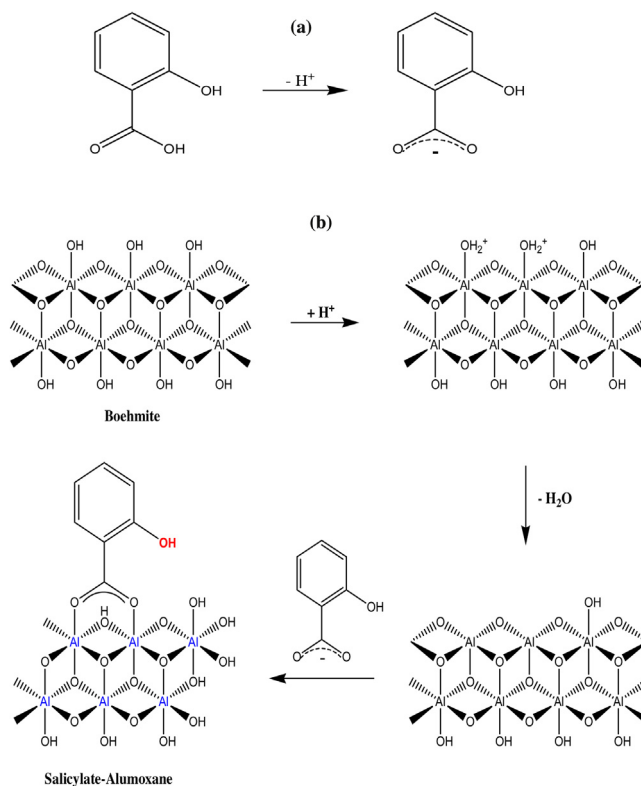

Fig. 1. (a) Deprotonation of salicylic acid and (b) reaction steps for the production of SA nanoparticles.

the deprotonation of salicylic acid and the production of salicylate alumoxane.

2.4. Preparation of SA/PS nanocomposite membranes

Neat and nanocomposite PS membranes were prepared using phase inversion induced by immersion precipitation. First, Triton X100 (2 wt.%) and PEG 400 (1 wt.%) were added to DMAc. Next, SA nanoparticles (0.1, 0.5, 1 and 2 wt.%) were added to three separate solutions and dispersed by an ultrasonic bath for 30 min. Triton X100 improves the dispersion of nanoparticles in the casting solution. After a complete dispersion of the nano fillers, the PS powder was added to the solution, and the mixture was stirred by a magnetic stirrer at 400 rpm for 12 h to form a uniform and homogeneous solution. Next, the polymer solution was kept motionless for 4 h to allow air bubbles to escape. The solution was then cast over a polyester non-woven fabric using a 75 μm-thick, casting knife and immediately immersed into a non-solvent bath containing distilled water and 0.1 wt.% SDS. SDS in the non-solvent bath influences the membrane morphology and performance. In particular, it improves membrane surface porosity and pore density, and consequently membrane permeability [37]. The fabricated membranes were washed with fresh distilled water several times to remove the residual solvent, followed by drying between two filter papers at room temperature. In this paper, we will call our membranes prepared with 0, 0.1, 0.5, 1 and 2 wt.% of SA nanoparticles UF-S0, UF-S0.1, UF-S0.5, UF-S1 and UF-S2, respectively.

2.5. Characterization of SA nanoparticles and membranes

To study the synthesized SA nanoparticles, transmission electron microscopy (TEM) (Zeiss – EM10C – 80 KV) was used. The thermal behavior of SA nanoparticles was investigated via thermogravimetric analysis (TGA-DCS1, Mettler-Toledo, S.A.E.) at a heating